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Contact piece made of tungsten provided with a corrosion-resistant layer made of tin

Due to its excellent burn-off resistance, of all high-melting metals tungsten is the metal of choice for use as a contact overlay in electromechanical switching devices whenever high switching sequences combined with considerable formation of sparks are at issue. Provided that the contact force is sufficiently high and a minimum switching voltage is given, tungsten contact pieces may be used free of trouble in various switching devices such as motor vehicle contact breakers, motor vehicle horns and relays. As a rule, the contact piece is manufactured as a rivet comprising a tungsten plate as a contact overlay soldered onto a rivet-shaped support made of soft iron or copper (cf. Fig. 1).

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Tungsten, however, is no noble metal. When switching is performed under air, oxidic coatings are to be expected at the surface. The formation of corrosion on tungsten contact pieces has been known to pose a problem for more than 50 years and under unfavourable switching conditions impairs the universal applicability of tungsten as a contact material. Under dry air and in hot environment (desert climate) the tungsten contact will remain unimpaired and fully functioning for a long period of time. If, however, the surroundings are accompanied by humidity (tropical climate), rapid corrosion of the unprotected tungsten will result.

The circumstances and effects of the formation of corrosion are described in the following publications:

Keil, A.:	Eine spezifische Korrosionserscheinung an Wolfram-Kontakten. Werkstoffe und Korrosion 7 (1952) 263-265.
Keil, A.:	Meyer, C.L.: Korrosionserscheinungen an Unterbrecherkontakten. Elektropost 7 (1954) 93-95.
Vinaricky, E et al.:	Elektrische Kontakte, Werkstoffe und Anwendungen, Berlin 2002, p. 178.

The publications report on contact malfunctions due to released organic substances, in particular under tropical conditions.

Recently, intense research has been conducted with respect to malfunctions with fanfares and signal horns in the motor vehicle supply sector due to corrosion of the contact pieces. The same applies to electromechanical relays the forerunning or main contacts of which are coated with tungsten.

Under warm and humid climate, tungsten contact assemblies tend to fail increasingly. This can be observed in a statistically striking way with horn contacts if, e.g., prior to launching the sales of a new motor vehicle type a specific number of motor vehicles is produced for the storage yard, possibly left to stand there for months under warm and humid conditions before being delivered to the customer via the car dealer.

In case a horn ceases to operate, upon opening the piece complained about, a thick oxide layer of tungsten oxide and tungstates often becomes apparent on and between the closed tungsten contact pieces. Due to this intermediate layer, the contacts become separated, the contact resistance gets high, the horn ceases to operate. Numerous efforts have been made to remedy this defect which is annoying to the customer and costly for the manufacturer:

A method generally known to the skilled person is to coat the entire contact rivet with a thin nickel layer prior to incorporating it into the switching device. Due to the passivation of nickel, the switched-off contact remains clean and free of corrosion layers for a long time if the nickel layer is intact. However, due to the necessary testing of the new horn at the horn manufacturer's, the Ni layer is partly destroyed at the switching surface. The protective effect of the Ni layer decreases considerably. In a field test, a positive effect of nickel-plating cannot be clearly proven any longer.

US-A-2,547,947 describes electric contact arrangements for ignition systems of internal combustion engines in which the movable part consists of a steel or iron arm onto which a tungsten contact plate is soldered or welded. In order to avoid the formation of dark colored deposits at the tungsten surface, the arrangement is plated with nickel, chromium, cadmium or zinc, the contact surface and its edges having been polished upon plating in order to remove plated metal from these areas of the tungsten surface.

Another possibility would be to carburize the tungsten switch surface. A tungsten carbide-containing hard layer some µm in thickness is formed. Without any doubt such a hard layer shows increased corrosion resistance.

Japanese patent publication 20128/1974 discloses the use of graphite powder as a carburizing agent.

German laid-open publication 3232097 A1 discloses the use of propane as a carburizing agent in the controlled-atmosphere furnace. In this context, an impairment of the solder side of the tungsten contact overlay by the concurrent undesired carburization as well as an impairment of the heating conductors of the furnace cannot be ruled out.

Moreover, in both methods the thin protective layer is destroyed by switching the horn on and the free tungsten in turn is exposed to the surrounding atmosphere without protection.

The preparation of such layers is costly and requires additional working steps, thus making it too expensive. In practice, tungsten contacts comprising hard layers could not prove themselves successful.

Further attempts to improve the corrosion resistance of tungsten contact rivets consisted in silver-plating the contact rivet or in using a soldering metal having a high silver content (thus, being a more noble metal) instead of the common copper solder.

These methods were also only used sporadically and did not bring about a drastic improvement in corrosion resistance.

German laid-open publication 3626144 A1 discloses a contact containing a silver base layer, an intermediate layer made of tin and an outer layer made of tungsten.

Thus, the object underlying the invention is to develop a contact piece consisting of a tungsten overlay soldered onto a metallic support by means of a Cu or Ag hard soldering metal, which contact piece does not exhibit impaired switching properties under corrosive conditions, in particular under the influence of a warm and humid climate.

This object was solved by the surprising finding that by covering the solder layer and the support with a thin tin layer, the corrosion resistance of the tungsten overlay can be considerably improved.

Thus, the subject matter of the invention is a contact piece comprising a tungsten overlay (1), the solder (2) and support (3) of which are coated with a thin layer (4) of tin.

Preferred embodiments of the rivet are the subject matter of claims 2 and 3. A method for the preparation of the contact piece is described in claims 4 to 7. With respect to the electrochemical series, tin differs only slightly from tungsten. However, in practice, as compared with the less noble metals Ni, Cr, Cd and Zn suggested in US-A-2,547,947, tin has proven to be particularly suitable. What is to be emphasized in connection with a galvanic deposition of Sn is that the latter is a method which can be carried out at a very reasonable price and gives an esthetically attractive result.

The inventive solution is advantageous in that in the switching contact the burn-off material tungsten is free of any protective/foreign layer and, thus, the latter can neither be destroyed by the formation of sparks nor other disturbing influences upon switching have to be reckoned with. The effect of the tin layer is not achieved via physically covering the tungsten to be protected, but is merely achieved by electrochemical means.

The inventors assume that by the formation of a local galvanic element under the inclusion of a liquid film on the respective surface, the tin preferably dissolves under the present potential ratios for the benefit of the more noble tungsten.

If more noble elements such as copper (as a Cu solder) or Ag (as an electrolytic cover) form a local galvanic element with W, the tungsten of the W-contact overlay will preferably dissolve as the so-called sacrificial anode. In view of the formation of a local galvanic element, Ag as a protective layer is counterproductive and copper as an adjacent solder layer even promotes corrosion. The same presumably applies to Ni which due to the displacement in potential behaves cathodically, i.e. more noble.

In the accompanying drawing:

Fig. 1 (schematically) depicts a contact piece for use as a horn and relay contact which consists of a tungsten contact overlay (1), soldered by means of Cu or Ag hard solder (2) onto a metallic support (3) which according to the invention is covered with a tin layer (4).

Fig. 2 depicts a contact overlay made of W on a rivet base, galvanically protected with 0.5 to 1 μm of a tin layer after corrosion testing.

Fig. 3 depicts a contact overlay made of W of a rivet in accordance with the prior art as a reference prior to corrosion testing.

Fig. 4 depicts a contact overlay made of W of a rivet in accordance with the prior art after corrosion testing.

The following non-limiting example illustrates a preferred embodiment of the invention:

Example

Contact rivets comprising a tungsten overlay 4 mm in diameter and 0,8 mm in thickness, soldered with Cu solder onto nickel-plated iron supports, are provided with a tin layer 0.2 to 2 μm in thickness which is applied galvanically. Subsequently, the tin only loosely adhering to the tungsten surface is removed mechanically by means of sliding grinding. The thus ready-to-supply contact rivets are subjected to a constant climate in the corrosion test:
48 h at 96% relative humidity and 50°C. During this test, about 20 pieces of the rivets provided with a tin layer as described above and exhibiting an exposed tungsten surface on a porcelain support are introduced into an exsiccator. The bottom of the exsiccator contains a saturated potassium sulfate solution on top of which the relative humidity is adjusted to 96%. On a separate porcelain support rivets in accordance with the prior art – without any additional galvanic base metal layer – are added as a reference. The exsiccator is temperature-controlled in a climatic test cabinet for 48 h at constant 50°C.

The result after 48 hours is depicted in Figures 2 and 4. As compared with the non-corroded standard (Fig. 3), the galvanically after-treated rivets show only slight

haziness at the contact surface. As regards the reference without galvanic after-treatment, however, the W-surface is covered with thick greenish-brown crusts which, starting from the periphery at the Cu solder, extend into the tungsten surface, in part up to its center. These crusts are probably inorganic salts of copper and tungsten. If these are located between the closed contacts of a horn, this will result in an increased contact resistance and, consequently, the break down of the horn.

CLAIMS

1. A contact piece comprising a tungsten overlay (1) soldered onto a metallic support (3) via a solder layer (2), characterized in that at least portions of the solder layer (2) and the support (3) are covered by a layer of tin (4).

2. The contact piece as claimed in claim 1, characterized in that the layer of tin is 0.1 to 20 μm thick.

3. The contact piece as claimed in claim 2, characterized in that the layer of tin is 0.2 to 2 μm thick.

4. A method for the preparation of a contact piece as claimed in any one of claims 1 to 3, characterized in that a layer of tin (4) is applied onto the contact piece and subsequently tin (4) which may be present on the tungsten overlay (1) is removed.

5. The method as claimed in claim 4, characterized in that the layer is applied via electroplating.

6. The method as claimed in claim 4 or 5, characterized in that the tin is applied selectively onto the solder and the metallic support.

7. The method as claimed in any one of claims 4 to 6, characterized in that the re-exposure of the tungsten overlay is carried out by sliding grinding.

8. Use of the contact piece as claimed in any one of claims 1 to 3 as a horn contact or a relay contact.

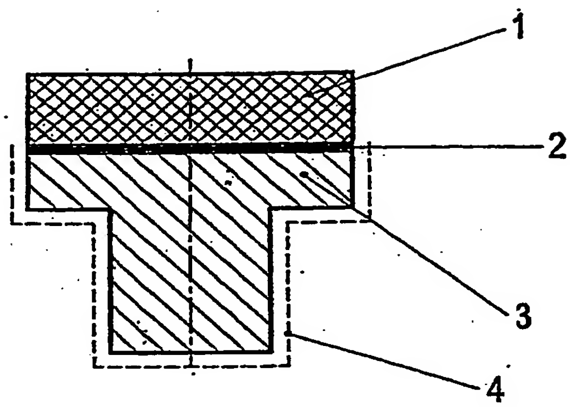

Fig. 1

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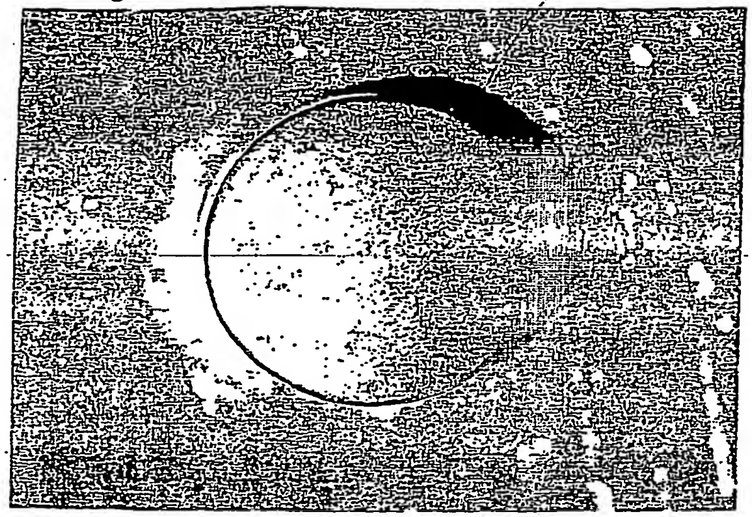
Fig. 2 shadow



Sn layer 11:1

Fig. 3

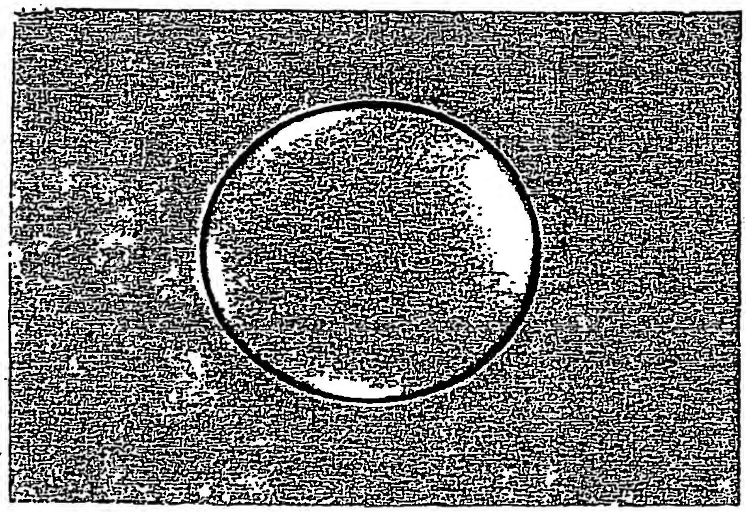


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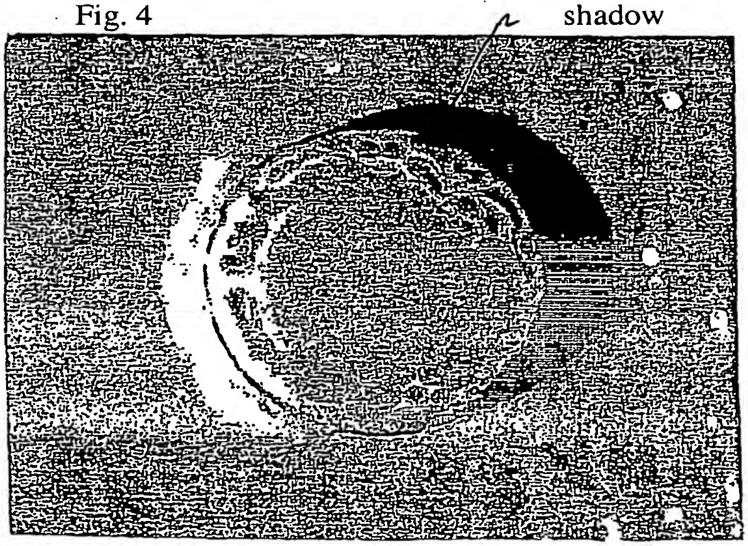
Fig. 4 shadow



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